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Hydrazine Detection Using Langmuir-Blodgett Films of a Nickel Dithiolene Complex on Chemiresistor Sensors

JAY W. GRATE, SUSAN ROSE-PEHRSSON AND WILLIAM R. BARGER

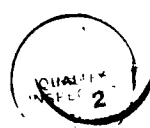*Surface Chemistry Branch*
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Films of bis(diethylaminodithiobenzil)nickel, BDN, can be spread on the Langmuir trough, but do not transfer uniformly to quartz substrates. Mixed films containing DBN and stearyl alcohol in a 1:1 molar ratio will transfer and are electrically conductive. Chemiresistor sensors were fabricated by depositing 5, 11, 21, 33, or 45 layers onto interdigital electrodes. The current through these sensors increases by three orders of magnitude on exposure to ppb levels of hydrazine, with high signal to noise ratios. Exposure to potential interferents such as ammonia at 29 ppm or 60% relative humidity at room temperature caused current increases of only 10 to 20 fold. These sensors are promising for use in alarm devices for hydrazine. The influence of the number of LB layers on sensor response characteristics has been examined.

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HYDRAZINE DETECTION USING LANGMUIR-BLODGETT FILMS OF A NICKEL DITHIOLENE COMPLEX ON CHEMIRESISTOR SENSORS

INTRODUCTION

Chemiresistor sensors represent a conceptually very simple electronic approach to the detection of chemical species in the gas phase. The current through a film of a semiconducting material is monitored while the material is subjected to a constant bias voltage and a varying ambient atmosphere. Changes in current observed when the film material interacts with specific vapors provide the mechanism for vapor detection. The film material is therefore the critical component of the sensor, since it determines the sensitivity and the specificity for a particular vapor or vapors. This material must be electronically conducting and applicable as a continuous film if it is to be useful on a chemiresistor sensor. The remainder of the sensor can be designed to fit the requirements of the material. For example, if the vapor sensitive material is a weakly conducting organic semiconductor, then the device is fabricated with a large number of electrode fingers in an interdigital array. This geometry, illustrated schematically in Figure 1, provides a short electrode spacing with a large electrode perimeter, facilitating the measurement of weak currents through resistive materials.

Organic semiconductors have shown great promise as chemiresistor coating materials because of their sensitivity to low concentrations of gases or vapors. In particular, phthalocyanines in the form of sublimed (1-4) or Langmuir-Blodgett (5-8) thin films, have been investigated by several groups. We now report initial results on an alternative class of organic semiconductors, the dithiolenes. Neutral dithiolene transition metal complexes were originally synthesized and investigated by Schrauzer and coworkers, (9-12) and were demonstrated to be electronic conductors (13). Numerous investigations have since been carried out, not only for their electrical behavior, but also because of their structural and electrochemical

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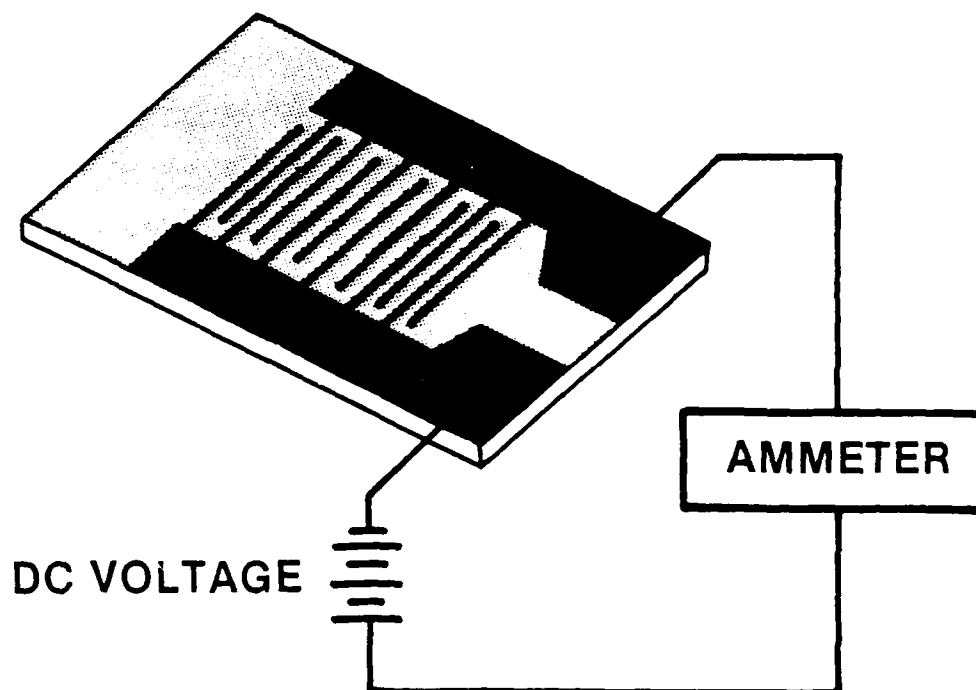# CHEMIRESISTOR DEVICE

Figure 1.   Schematic diagram of a chemiresistor sensor; the gray area on the device

is a thin film of an organic semiconductor.

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properties, useful spectral characteristics, and interesting molecular orbital structure (14-25). These compounds appeared attractive to us as potential chemiresistor coating materials because of their known conductivity, an essential property for this type of sensor.

In this study, we focus on three aspects of chemiresistor vapor sensors. First, we introduce the use of a dithiolene complex as the vapor sensitive component on a microelectronic chemical sensor. To our knowledge, these materials have not been previously reported for this application. Bis(diethylaminodithiobenzil)nickel, or BDN, shown in Figure 2, is investigated as the prototype compound (23-25). Second, we explore the use of the Langmuir-Blodgett technique for preparing very thin films containing this material. This technique affords the advantages of precise control over film thickness, and the influence of this parameter on sensor performance has been investigated. Third, we demonstrate that the sensors are both highly sensitive and selective for the detection of ppb levels of hydrazine in the gas phase. Hydrazine (N_2H_4) and methyl-substituted hydrazines are useful as industrial chemicals, and as propellants for missiles and thruster rockets, but their toxicologic properties are of great concern. The ability to monitor atmospheric concentrations and to detect leaks is therefore important for insuring safe working conditions where hydrazines are in use.

EXPERIMENTAL

Materials

Bis(4-diethylaminodithiobenzil)nickel, (or bis[1-[4-(diethylamino)phenyl]-2-phenyl-1,2-ethenedithiolato(2-)-S,S']nickel), "BDN", was purchased from Kodak (Assay by UV/Vis 98% min. TLC no detectable impurities). It is not known if this material is the cis- or trans- isomer or a mixture, but a mixture is likely. It was recrystallized by layering hexane over a chloroform solution and
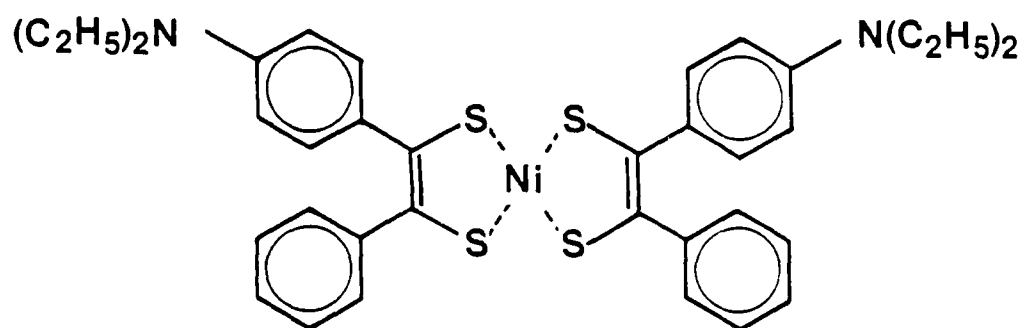
Figure 2.   The structure of bis(4-diethylaminodithiobenzil)nickel, BDN.   The
diethylamino-substituents may be cis or trans.

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recovering the dark green needles after a few days of solvent diffusion. Stearyl alcohol, 99.5%, was purchased from Lachat Chemicals Incorporated and used as received.

Propellant grade hydrazine, monomethylhydrazine(MMH), and unsymmetrical or 1,1-dimethylhydrazine(UDMH), were obtained from Olin Chemicals. Ammonia was purchased as a calibrated gas mixture from Matheson.

<u>Substrates</u>

The chemiresistor devices used were identical to those described in reference (6) consisting of a set of gold interdigital electrodes on a quartz substrate(5mm x 8mm), with 40 finger pairs, 20 microns wide, spaced 20 microns apart, and having a finger overlap distance of 3200 microns. These devices were cleaned with hot chloroform in a Soxhlet extractor immediately prior to coating.

Quartz slides(5 cm X 2.5 cm X .1 cm) were purchased from Thomas Scientific(6686-U20), cleaned in hot HNO_3 for a few minutes, rinsed with water, and then cleaned with chloroform in a Soxhlet extractor.

<u>Spectra</u>

Absorbance measurements were made on a Perkin-Elmer Lambda 5 UV Visible Spectrometer.

<u>Langmuir-Blodgett Apparatus and Method</u>

Film pressure vs. area isotherm measurements and film depositions were carried out at $25^{O}C$ using a thermostatted, paraffin-coated, Langmuir trough constructed in our laboratory and interfaced with an Apple IIe microcomputer. Surface tension measurements were made with a Gould UC-2 strain gauge carrying a 1.7 cm wide platinum foil Wilhelmy plate. Motors for controlling bar movement(to put pressure on the film) and for substrate dipping were operated automatically with the computer. More details on the trough can be found in reference (26).

Water used as the subphase was triply distilled, with the last two distillations from an all quartz still. Solutions of BDN, and of BDN:stearyl alcohol 1:1 mole ratio, were

prepared in Fischer ACS chloroform, typically 0.5 mg/ml in BDN. All film transfer operations began with the substrate submerged. The dipping velocity was 4.2×10^{-4} m/sec, with the device being coated allowed to dry in air for 5 minutes after each down-up cycle.

Electrical Measurements

All electrical measurements were made using a Kiethley 617 programmable electrometer, with the data transferred to a microcomputer using the IEEE-488 bus.

The resistances of the devices were measured by stepping the applied voltage, using the voltage source on the electrometer, from 0 to +1.25 volts, back down to -1.25 volts, and back up to 0 volts, by 0.05 volt steps, and measuring the current(electrometer in AMPS mode) after each step. The time interval between steps, necessary for the electrometer to settle on the new current, was ten seconds in most cases, but could be reduced to five seconds for the least resistive devices. The device whose resistance was being measured was contained in a molded Teflon container, with a gas inlet for dry air or nitrogen. The 100 mL/min. gas flow escaped via gaps at the container lid. The container was also fitted with two gold plated clips held in place with two screws, to make electrical contact with the devices. The screws extended through the bottom of the container. One screw was connected to a BNC cable connected to the voltage source of the electrometer. The other screw was connected via a triaxial cable to INPUT HI of the electrometer input. INPUT LO and ground were grounded. The sensor, container, and connections were shielded in a closed die cast aluminum chassis box connected to ground. Using this set up, IV curves measured with no device installed were essentially flat, with resistances of at least 1000 teraohms, and an offset current of .01 picoamps.

Current measurements during vapor exposures were made at a constant bias voltage of 1 volt, with up to five sensors contained in a specially designed chamber. Each sensor was connected via gold plated clips and a triaxial cable to a Kiethley 705 Scanner equipped with a Model 7058 low current scanner card, whose single output was connected

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via triaxial cable to the electrometer. The bias voltage was supplied by the electrometer via a BNC cable.

Vapor Exposures

Hydrazine has a strong tendency to adsorb on surfaces and on many surfaces it will decompose. This factor must be taken into account when designing experiments utilizing ppb concentrations of this vapor. Therefore, all vapor streams were generated using dynamic methods (27) in order to equilibrate tubing walls, and the sensor test chamber was designed to deliver the vapor stream directly to the surface of the sensor without any opportunity to interact with chamber walls first. The chamber for vapor exposures consisted of a machined and anodized aluminum box, an insulating platform inside on which to mount and connect the sensors, and a glass manifold to deliver gas to the sensors in parallel. The manifold was designed to divide a single incoming gas stream into five parts and deliver each directly to the surface of a sensor. The aluminum box was grounded and provided electrical shielding for the sensors.

Air streams at known relative humidity and hydrazine propellant concentration were produced using the apparatus described by Rose and Holtzclaw· (28). This system constructed of glass and teflon consists of a diffusion tube source of hydrazine, monomethylhydrazine(MMH), or 1,1-dimethylhydrazine(UDMH), a 5 L/min source of zero-grade air which could be humidified to the desired level, and two pyrex gas manifolds connected by a three-way solenoid valve. One manifold contained a flow of clean air and the other clean air plus test vapor. Gas flows were controlled by mass flow controllers(Matheson Gas Products).

The hydrazine source consisted of a diffusion tube contained in a glass impinger in a constant temperature bath. A 100 mL/min. flow of dry nitrogen through the impinger swept the hydrazine vapor into a known flow of air (approximately 5 L/min.) at known relative humidity. This vapor stream flowed through one of the manifolds of the apparatus described above. Vapor streams containing MMH and UDMH were generated

similarly. By adjusting the temperature of the diffusion tube and the amount of dilution air, concentrations of hydrazine, MMH, and UDMH could be controlled to +/- 10% over the 20-2000 ppb range.

Hydrazine vapor concentrations were verified using impinger collection of the vapor stream and analysis by NIOSH wet chemical methods (29). In addition, a MDA Model 7100 Hydrazine Detector (MDA Scientific, Inc.) was used to measure the hydrazine concentration in the vapor stream.

Consistent delivery of hydrazine to the five positions within the sensor test chamber was tested in two ways. In the first test, 1.6 L/min. of dry air containing 80 ppb hydrazine were pushed through the test chamber for 60 minutes. Citrate coated substrates from the NRL hydrazine dosimeter badge (30) located in each of the five sensor positions were then analysed by coulometric titration with amperometric detection (31). Each substrate had captured within 12% the expected quantity of hydrazine. In the second test, approximately 1 L/min. of hydrazine containing air was pulled through the test chamber using a personal sampling pump attached to the gas outlet. Dosimeter badge substrates located in the sensor positions were again analysed and the accuracy and spread of the results were within +/-12%.

Sensors were tested against hydrazines using a gas flow rate of 1000 mL/min. drawn through the chamber by the sampling pump connected to the outlet of the chamber(giving 200 mL/min. over each of the five sensors). The gas could be switched between clean air and hydrazine contaminated air using teflon solenoid valves.

Gas streams containing ammonia were generated by mixing known flow rates of the calibrated gas mixture with known flow rates of air. Humid air was generated at room temperature by bubbling the air through a five gallon container of distilled deionized water. The relative humidity was controlled by mixing known flow rates of this air with known flow rates of dry air, and was measured with a Hygrodynamics hygrometer. Sensor testing against humid air was conducted using both delivery methods, pushing and

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pulling the test gas through the test chamber. Sensor testing against ammonia was conducted by pushing 1000 mL/min. of gas through the test chamber. The gas stream could be switched between clean air and test vapor using solenoid valves as above.

RESULTS

Langmuir-Blodgett Film Studies

Prior to evaluating sensors based on a given material, it is first necessary to have a means to apply films of the material to the sensor surface. For chemiresistors, it is neccessary for the film to be continuous, so that it can carry electrical current, and that the means of preparing this film be easily controllable and reproducible. In addition, for gas sensing it is useful to have very thin films to permit facile interactions with gases, and rapid response and recovery times. The Langmuir-Blodgett method satisfies these requirements if the material will form films at the air-water interface of the Langmuir trough, and if these films will transfer to the sensor substrate.

Therefore, the ability of bis(diethylaminodithiobenzil)nickel (BDN) to form films at the air-water interface of a Langmuir-Blodgett (LB) trough was investigated first. Films prepared by spreading a chloroform solution of pure BDN on the waters surface and compressing to 20 millinewtons/meter surface pressure were visually inhomogeneous and somewhat rigid. Nevertheless, the force area plots were reproducible and an example is shown in Figure 3. The small apparent area per molecule observed, only 12 $Å^2$, indicates that the molecules are aggregated or stacked, and that the films were not a single molecule thick.

Attempts to transfer films of pure BDN from the air-water interface to quartz substrates by the LB vertical dipping technique were unsuccessful. This behavior has also been observed in our laboratory with various substituted phthalocyanines, but could be overcome by mixing the phthalocyanine with stearyl alcohol (6,26). Mixtures of BDN with stearyl alcohol in a 1:1 molar ratio gave films which were visually homogeneous, and
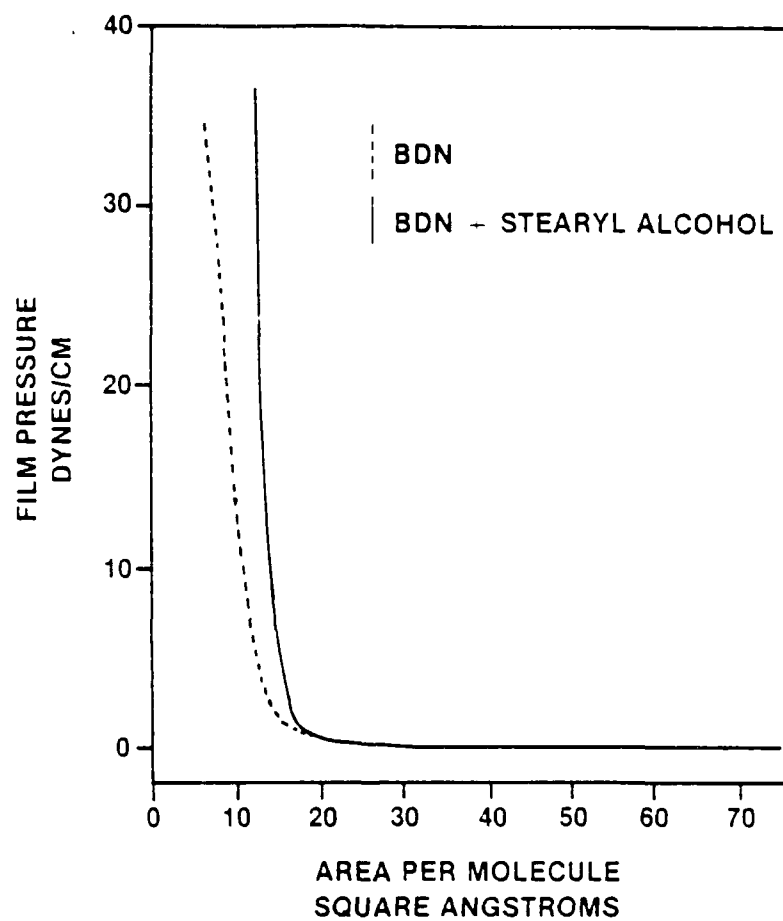
Figure 3. Force-area curve for BDN and its mixture with stearyl alcohol on the Langmuir trough.

could be transferred to flat quartz substrates. Therefore, mixed films were used throughout the remainder of this study. The force-area curve of a mixed film is shown in Figure 3. The observed average area per molecule of 15 $Å^2$ is between the 12 $Å^2$ observed for pure BDN, and the 20 $Å^2$ usually observed for stearyl alcohol and other linear fatty molecules. Again, this result indicates that these films are not classical monomolecular LB films. Nevertheless, the technique remains useful for reproducibly depositing very thin films.

The behavior of compressed films on the water surface was examined before studying their transfer to solid substrates. The surface pressure of freshly spread films compressed to 20 dynes/cm would slowly decrease over the course of an hour. To maintain the pressure at 20 dynes/cm, the bar on the LB trough would occasionally move forward to decrease the area of the film. A more stable film could be produced by expanding this film and recompressing it. The area per molecule was reduced to 14 $Å^2$. An additional expansion and recompression gave a stable film again with an area per molecule of 14 $Å^2$. In a single experiment to determine if molecular reorganization might occur slowly on the water surface, a fresh film was spread and left uncompressed for 10 hours. The first compression to 20 dynes/cm gave a very stable film with a slightly larger area per molecule of 16 $Å^2$. These results suggest that some reorganization does occur on long standing, but this is not a practical procedure to follow when producing coated substrates.

Film transfer was investigated by using the conventional LB dipping method to coat 5 cm by 2.5 cm quartz slides. Comparing the decrease in the area of the film on the air-water interface with the area of quartz substrate passing through this interface (the transfer ratio) provides a measure of the efficiency of transfer. The procedure began with the quartz slide below the surface, and the film was always stabilized by repeated compression prior to dipping, as described above. In four separate experiments, the measured transfer ratio on the first pass (upward) was between 94% and 112%. The

second pass (downward) gave consistently poor transfer ratios, ranging from 31% to 50%. However, the third pass (upward) and nearly all subsequent upward passes gave ratios near 100%. The fourth pass (downward) and all subsequent downward passes gave transfer ratios better than the second pass (downward), but still less than 100%, typically 75% to 90%.

The consistency of transfer was also checked by measuring the optical absorbance of the films on the quartz substrates as function of the number of layers deposited. These spectra were similar to those of solutions of the dithiolene complex in chloroform. Absorbance data on the deposited films were collected on the peak at 321.5 nm and are plotted in Figure 4; note that 30 layers represents 15 passes through the air-water interface, coating both sides of the slide. It is clear that the amount of material on the slide is linearly proportional to the number of LB layers, confirming the use of the LB technique for the reproducible deposition of very thin films of this material.

Sensor Fabrication and Electrical Characteristics

Chemireristor sensors using BDN as the chemically sensitive component were fabricated by coating bare chemiresistor devices with thin films of BDN and stearyl alcohol as described above. The interdigital fingers on the devices were constructed of gold to insure ohmic contact with the organic film. The number of LB layers on the devices were varied to determine the influence of film thickness on electrical properties and sensitivity to gases. Thus, sensors were prepared with 1, 5, 11, 21, 33, and 45 layers, and typically 3 sensors of each thickness.

The baseline d.c. electrical conductivities of these sensors were determined by measuring the current passing through them as a function of the bias voltage applied to the interdigital fingers. These IV curves were measured between -1.25 and +1.25 Volts, in the dark, under a stream of dry nitrogen at room temperature. A typical result is illustrated in Figure 5. The curves were linear with no hysteresis, confirming that the device is functioning as a simple resistor with ohmic contact between the film and the
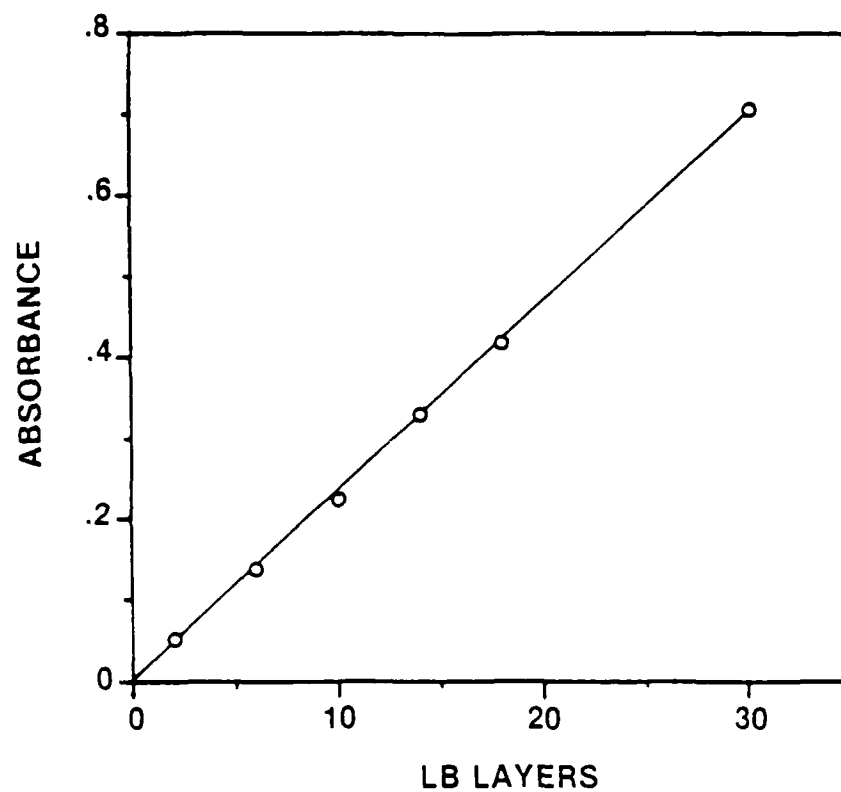
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Figure 4.   Optical absorbance vs. the number of LB layers deposited, demonstrating that the LB method allows precise control of the amount of BDN applied.
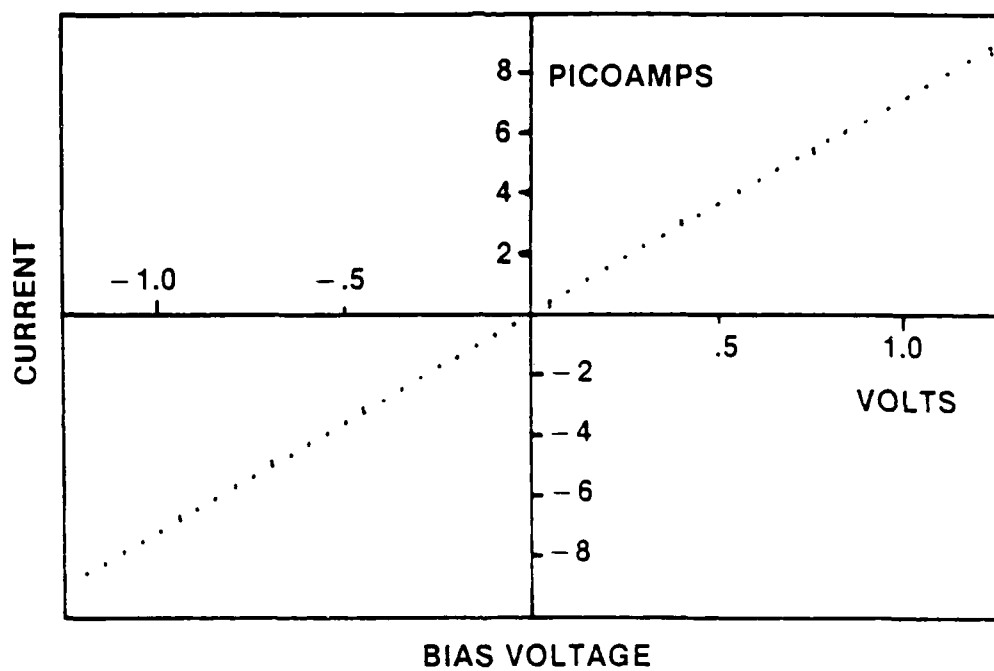
Figure 5.   IV characteristic for a chemiresistor sensor with 21 LB layers of BDN and

stearyl alcohol; the slope gives a resistance of 0.14 teraohms.

fingers. The slope of the line gives the resistance. The resistances of these devices are not influenced by changing the atmosphere from dry nitrogen to dry air, but are influenced by the presence of gases such as ammonia, water, and hydrazine.

The results of IV curve measurements under dry nitrogen are shown in Figure 6, which plots the resistances of these sensors as a function of the film thickness in LB layers. The resistance of each sensor was measured repeatedly (usually ten times) to determine its drift, and this is represented by a vertical bar. Data for sensors with only one LB layer are not plotted since these had resistances of 100 teraohms or greater. Resistance decreases rapidly on increasing the number of layers from 5 to 21. Beyond 21 layers, the resistance continues to decrease but not as rapidly. This provides a basis for deciding on how to trade off between baseline conductivity, with higher conductivities being easier to measure, versus keeping the gas sensitive layer as thin as possible to maximize the speed with which the film responds and recovers from exposures to detectable gases.

Sensor Responses to Hydrazine (N$_2$H$_4$)

Sensors were tested for their responses to gases by alternately exposing them to a clean carrier gas, usually dry air, and carrier gas containing a calibrated concentration of the test gas. All tests were carried out with a low 1 V bias across the sensor, and currents were originally measured using an electrometer operational amplifier circuit of the type described in reference (7). Initial experiments using sensors coated with 45 LB layers demonstrated that thin layers of BDN are indeed gas sensitive, responding to water at 5000 to 10,000 ppm, and to ammonia at 10 to 100 ppm. The responses were rapid and reversible. We then examined the possibility of using these devices for the specific problem of detecting hydrazine at ppm - ppb levels. Nickel dithiolene complexes are known to react in solution with stoichiometric or excess quantities of liquid hydrazine, giving reduced products (11). The ability of trace amounts of hydrazine in the gas phase to influence the conductivity of thin dry films of a nickel dithiolene
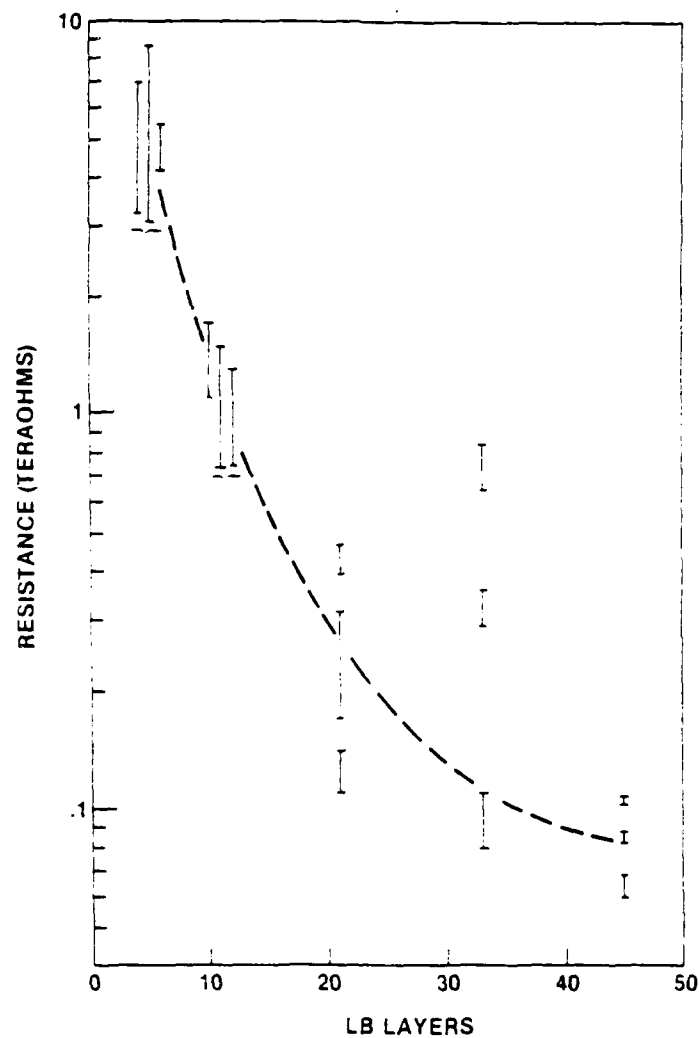
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Figure 6.   The resistances of chemiresistor sensors plotted as a function of the number of LB layers applied to the device.

complex was unknown, but clearly worth investigating. The first exposures to hydrazine demonstrated the validity of this approach, with hydrazine sensitivity far exceeding that of water or ammonia. Indeed, a mere 1 ppm of hydrazine in dry air produced increases in current of at least two orders of magnitude, albeit with slow recovery time. The response levels and recovery were largely unaffected by using humid air (55% RH) as the carrier gas. Sensitivities to monomethylhydrazine(MMH) and 1,1-dimethylhydrazine(UDMH) were also observed, with responses to hydrazine>MMH>UDMH.

The large current changes observed in these experiments could not be conveniently followed using a fixed gain electrometer op amp circuit. We therefore replaced this circuit with an autoranging programmable electrometer, as described in the Experimental section. All numerical results reported were measured with this system. In addition, we examined sensors with fewer numbers of layers, i.e. those described above, with 1, 5, 11, 21, and 33 LB layers, and which had no previous history of gas exposures except ambient air. These five sensors were tested simultaneously in one gas exposure chamber. The sensor with only 1 layer did not respond to gases and will not be discussed further.

Figure 7 illustrates the results of the first two exposures to hydrazine. The experiment began by following the baseline currents under dry air for 30 minutes. These initial currents illustrate again that conductivity increases with the number of LB layers on the sensor, in a non-linear fashion, as noted from the IV characteristics. Then the gas was changed to dry air containing 0.5 ppm of hydrazine for 20 minutes, switched back to clean dry air for 40 minutes, followed by hydrazine again for 20 minutes, and clean air for another 40 minutes. The currents observed are plotted on a log scale to illustrate the full magnitude of the response. Exposure to hydrazine produced an immediate two order of magnitude increase in current within two minutes(sampling every 40 seconds), an enormous response for such a minute concentration of gas. The data collected immediately upon this first exposure are presented in Table 1, as log I_t/I_0,
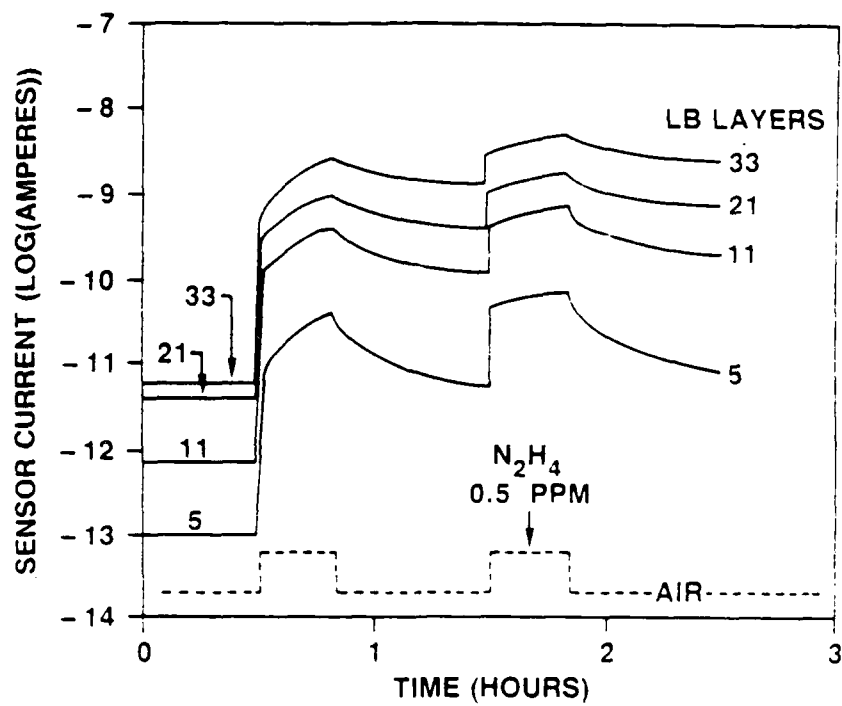
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Figure 7.   The responses of sensors with varying numbers of LB layers to 0.5 ppm

hydrazine in dry air, plotted on a log scale.

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Table 1. Current Changes Illustrating Rapid Initial Responses of New Sensors to 0.5 ppm Hydrazine

5 LB LAYERS		11 LB LAYERS		33 LB LAYERS	
t,sec[a]	$\log I_t/I_0$[b]	t,sec	$\log I_t/I_0$	t,sec	$\log I_t/I_0$
15	.72	22	1.81	38	1.75
55	1.89	62	2.13	78	1.90
95	1.94	102	2.19	118	1.97
135	1.99	142	2.24	158	2.02
3.75hr[c]	2.97	3.75hr	3.16	3.75hr	3.09

a   Seconds after changing dynamic air stream from dry air to dry air containing 0.5 ppm hydrazine.

b   Change in current, where I_0 is the baseline current in amps under dry air and I_t is the current in amps at time t observed under hydrazine.

c   Continuous long exposure to hydrazine to determine equilibrium response.

where Io is the current in amps measured just prior to hydrazine exposure, and I_t is the current at time t.

The initial rapid response to hydrazine is followed by a slower current increase, which is best examined when the data are plotted on a linear scale, as shown in Figure 8 for the 5 LB layer device. After 20 minutes of exposure, the device has not reached a stable equilibrium response, and recovery is slow on removing the hydrazine. The second exposure produces an immediate rise to the final level of the first exposure, followed by a continued slow increase in current. Equilibrium is nearly, but not completely, reached after another twenty minutes under hydrazine. Returning to Figure 7, it can be seen that the sensors with the fewest layers have an intial recovery that is faster that those with more layers. IV curves were run on these devices after these exposures. The characteristics were still linear, confirming that the coating material after hydrazine exposure is still an electronic conductor with ohmic contact with the electrodes.

Later on the same day, the sensors were exposed to a continuous 0.5 ppm concentration of hydrazine for 3 hours to determine the final equilibrium currents, I_{eq}. After a four day recovery under dry air, this experiment was repeated. The response curves from this experiment are shown in Figure 9. The initial current levels can be compared with those in Figure 7 to see the extent of recovery since the exposures four days previously. Only the 5 LB layer sensor recovered to near its initial level, while the remaining sensors still had currents which were ten times their pre-exposure levels. The 5 LB sensor was also the fastest to respond, requiring ca. 1 hour to reach its equilibrium level, while the 33 LB layer sensor required over 2 hours to reach equilibrium. The final I_{eq} values from the two long exposures to 0.5 ppm hydrazine were similar, indicating that equilibrium current levels are a reproducible response measurement. These current levels are given in Table 2. This is an important observation, since the initial baselines(I_0) are variable due to slow recovery, and expressing response as I_{eq}/I_0 would not be
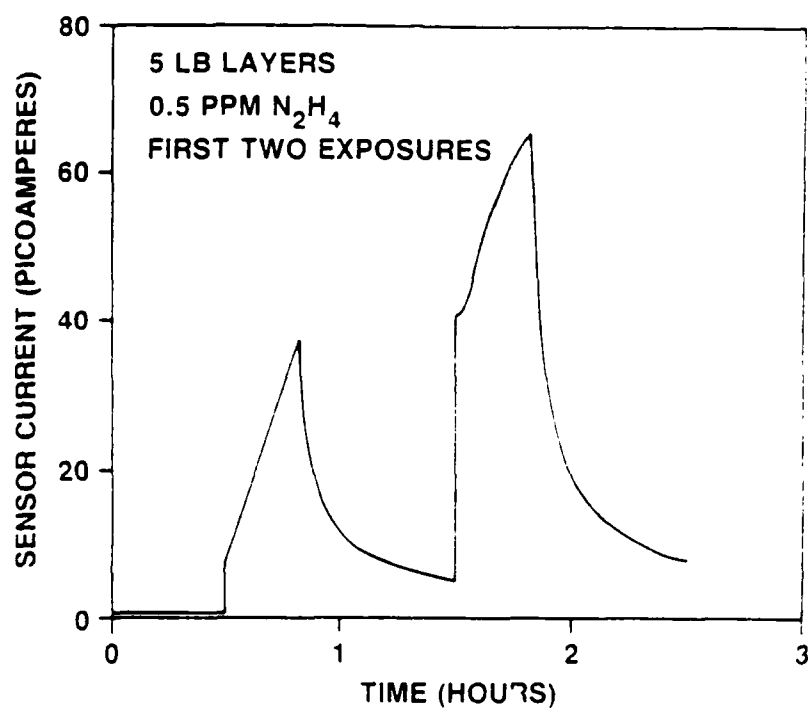
Figure 8.   The response of the 5 LB layer sensor to 0.5 ppm hydrazine in dry air, plotted on a linear scale.
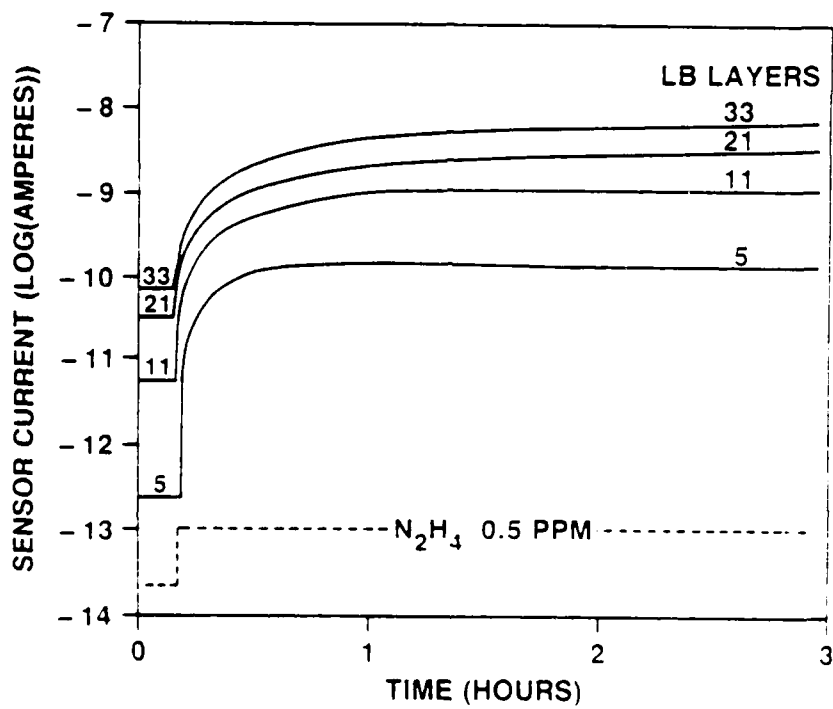
Figure 9. The equilibrium responses of sensors with varying numbers of LB layers to 0.5 ppm of hydrazine on day 4 of testing.

Table 2. Reproducibility of the Equilibrium Responses of New Sensors to 0.5 ppm Hydrazine

	5 LB LAYERS	11 LB LAYERS	33 LB LAYERS
Baseline Current, $\log I_0$ [a]	-13.04	-12.17	-11.23
1st Equilibrium Current, $\log I_{eq}$ [b]	-10.07	- 9.01	- 8.14
2nd Equilibrium Current, $\log I_{eq}$ [b]	- 9.85	- 8.96	- 8.13

[a] I_0 is the baseline current in amps under dry air.

[b]   Continuous long exposure to hydrazine (3.75 hr) to determine equilibrium response, I_{eq}, in amps.

reproducible. Therefore all responses are expressed as observed equilibrium currents, Ieq, without further calculation.

The overall behavior for all 0.5 ppm hydrazine exposures described thus far are illustrated for the 5 LB sensor in Figure 10. This figure includes recovery data collected for 15 hours after each equilibrium exposure. In addition, it provides a better view of the approach of equilibrium in the first 20 minute exposures, and the reproducibility of the equilibrium current levels in these first experiments.

Another observation from these experiments was that the 5 LB layer sensor response on long hydrazine exposure would begin to drift downward slightly after reaching its maximum equilibrium level. This result can be seen in Figures 9 and 10. This effect was also seen later for both the 5 and 11 LB layer sensors on exposure to a higher 1 ppm hydrazine concentration, with the effect being greater for the thinner sensor coating.

The overall history of vapor exposures for the 5, 11, and 33 LB layer sensors, including those experiments described above and subsequent experiments, are given in Table 3. (The data for the 21 LB layer sensor fall in between those of the 11 and 33 layer sensors and do not provide any additional information.) The data are presented in complete chronological form because hysteresis can be a concern with these types of sensors. For each exposure, the current immediately prior to exposure is given, measured either by an IV curve or from the initial current data prior to exposure. These values indicate the degree of recovery of the sensor from past exposures. It can be seen that the 5 LB layer sensor recovers to near its initial levels if given several days without hydrazine exposures, whereas the sensor with 33 LB layers does not. One month after the last exposure in the table, IV curves were run again. The sensors had been under dry air during this time, and recovery to initial current prior to any exposures was finally achieved. The baseline currents in the table are followed by the final response current measured at the end of the each gas exposure. In most cases these are
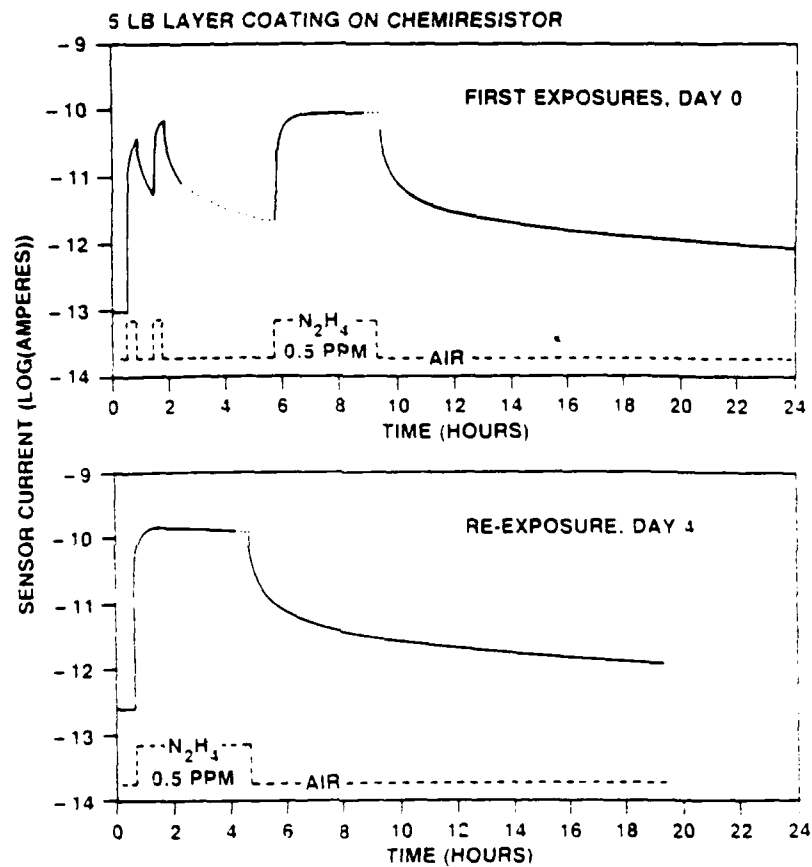
Figure 10.   The overall history of response and recovery of the 5 LB layer sensor for the first 5 days of testing. The solid lines are actual data, whereas the dotted lines are interpolated.

Table 3. Testing Sequence and Results for Exposures[a] of BDN Coated Sensors to Hydrazine, Ammonia, Water, MMH and UDMH

Gas	ppm	Day	5 LB LAYERS Picoamps[b] Baseline[c]	Response	11 LB LAYERS Picoamps Baseline	Response	33 LB LAYERS Picoamps Baseline	Response
N_2H_4	.5[d]	0	.09	66[e]	.67	670[e]	5.7	4500[e]
"	.5	0		86		970		7200
"	.5	4	.25	140	5.8	1100	74	6800
"	1.0	5	1.2	190	20	1500	390	9000
"	.2	6	1.2	26	17	250[f]	320	1700[f]
"	.4	7	1.1	43	17	420	410	2700[f]
"	1.4[g]	14	.18	94	3.0	960	58	5800
"	.5[g]	17	.46	14	8.8	160[f]	99	1100[f]
NH_3	29[d]	22	.17	.81[e]	3.3	14[e]	71	170[e]
"	29	22	.26	.91	6.7	16	110	210
H_2O	60%RH[d]	23	.12	1.8	2.6	14	59	120[e]
"	60%RH[d]	23	.12	1.7	2.6	11	67	110[e]
N_2H_4	.5	24	.13	41	3.0	480	76	3700
MMH	.5[h]	29	.26	5.2	6.0	130	79	1400
"	.5[h]	31	.24	4.5	13.	121	170	1300
UDMH	.5[h]	34	.31	.67	9.0	18	119	220

a   Typically 3-4 hour exposures to determine equilibrium responses, exceptions noted.

b   1 volt bias potential applied.

c   Baselines determined from either an IV curve measurement or current data collected just prior to exposure.

d   Response determined from the second of two twenty minute exposures.

e   Not a maximum equilibrium response.

f   Nearly, but not quite equilibrium.

g   Concentrations in some doubt due to erratic hydrazine generator behavior during this testing period.

h   Long exposure overnight

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equilibrium values, I_{eq}. Thus, the second and third rows of data in Table 3 give the I_{eq} values in response to the 0.5 ppm hydrazine exposures described above.

Final I_{eq} values were demonstrated to be dependent on gas phase hydrazine concentration by exposing the sensors to 1.0 ppm, 0.2 ppm and 0.4 ppm hydrazine, in that order, on consecutive days after the last 0.5 ppm exposure. This is not sufficient time for the sensors to fully recover from past exposures, so hysteresis is of some concern. Nevertheless, increasing or decreasing the hydrazine concentration caused the equilibrium response levels to increase or decrease in a fashion consistent with a linear relationship between current and concentration. The results for the 11 LB sensor are illustrated in Figure 11. However, subsequent exposures to 1.4 and 0.5 ppm hydrazine fell well below the calibration line. Unfortunately, during this period of testing, the hydrazine generator underwent inexplicable changes in output, ultimately requiring replacement of the hydrazine source and recalibration. The data for these 1.5 and 0.5 ppm exposures are therefore suspect. A later exposure, day 24, to 0.5 ppm hydrazine gave responses which were closer to the calibration line, but still less than the responses to 0.5 ppm hydrazine observed in the first 5 days. There is the suggestion in these results that a hysteresis may exist which manifests itself as a slight decrease in sensitivity on repeated exposure. However, more definitive experiments are required to test this possibility.

Sensor Responses to Ammonia, Water, MMH and UDMH

Exposures to potential interferents, first ammonia, then water, began on day 22, with five days of recovery from the last hydrazine exposures. Ammonia is a decomposition product of hydrazine and is produced biologically, whereas water is a potential problem because of humidity. Responses to 29 ppm of ammonia were slow and required roughly 3 hours to reach equilibrium. The important result is that response levels at this high ammonia concentration (25 ppm is the Threshold Limit Value) are 100 to 33 times less than the responses to 0.5 ppm hydrazine in the first experiments. The sensor with the fewest layers gives the best selectivity. Responses of most of these
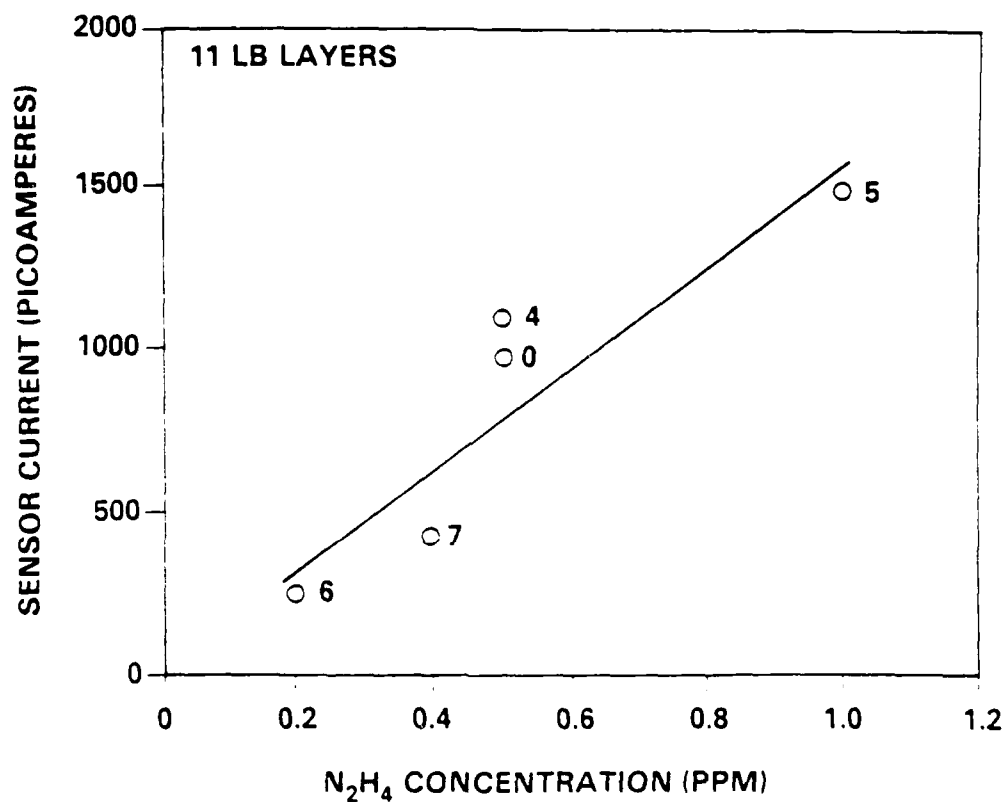
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Figure 11. The influence of hydrazine concentration on equilibrium response currents for the 11 LB layer sensor plotted on a linear scale. Numbers next to the data points indicate the day of testing. Only those results from the first seven days of testing are shown.
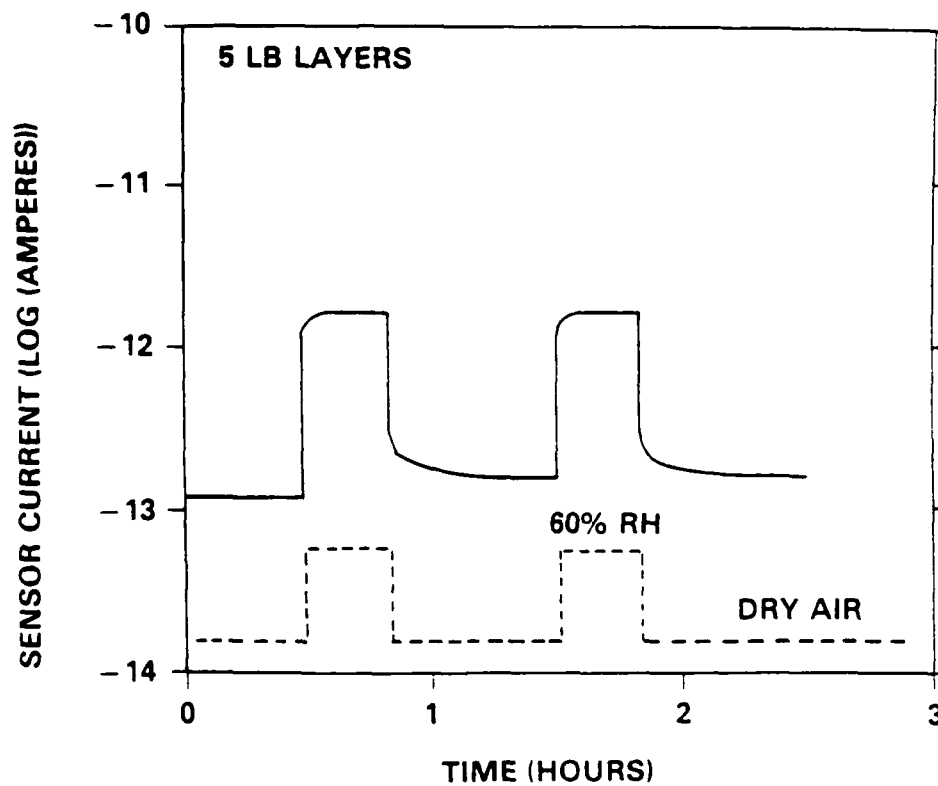
Figure 12.   The rapid responses of the 5 LB layer sensor to water vapor at 60%

relative humidity, plotted on a log scale.

sensors to water at 60%RH were rapid and rapidly reversible, as shown for the 5 LB layer sensor in Figure 12. (The 33 LB layer sensor was anomolous and gave slow responses and recovery.) The response levels were similar to those observed on exposure to 29 ppm ammonia. Again, the important result is that the responses to this very high concentration of water (on the order of 19000 ppm) were roughly 70 to 60 times lower than those observed on exposure to 0.5 ppm hydrazine. Thus, the selectivity between hydrazine and water is enormous (on the order of 10^6).

The last rows of data in Table 3 show the selectivity between hydrazine, MMH, and UDMH, all at 0.5 ppm. Responses to the latter two gases were slower than hydrazine, and current levels at 3.75 hours were not quite at equilibrium. Exposures were continued overnight and these equilibrium levels are reported in the table. The response to MMH was determined twice and was reproducible. As had been initially observed, these sensors respond most strongly to hydrazine. The reponse levels at 0.5 ppm UDMH were similar to the response levels at the higher concentrations of ammonia and water. Responses to MMH were approximately seven times higher than those to UDMH, but still less than those to hydrazine.

Baseline Noise and Projected Hydrazine Sensitivity

The results above demonstrate that these sensors are extremely sensitive to hydrazine, and responses to concentrations as low as 200 ppb have been demonstrated. By examining signal to noise ratios, one can project the ability of these sensors to detect even lower levels of hydrazine. Because these sensors were slow to completely recover from hydrazine exposures, baseline signal and noise levels have been determined from the data taken prior to the first exposure to 0.5 ppm hydrazine, day 0. A linear regression was run on 44 data points collected over 30 minutes. The standard deviation of the residuals was taken as the root mean square noise. These results are reported in Table 4. Signal to noise ratios of the baseline currents range from 110 to 2300. These

Table 4. Noise and Drift in the Initial Baseline Currents.[a]

LB Layers	Baseline Current picoamps	Noise[b] picoamps	Drift[c] picoamps/hour	Current/Noise
5	.089	.00082	.00020	110
11	.665	.00236	.0294	280
21	3.56	.00319	.202	1100
33	5.72	.00249	.295	2300

a   Determined from a linear regression on 44 data points collected over 30 minutes prior to first hydrazine exposure.

b   Determined from the standard deviation of the residuals.

c   Determined from the slope.

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Table 5. Noise Levels on Exposure to 200 ppb Hydrazine

LB Layers	Current[a] picoamps	Noise[b] picoamps	Current/Noise[c]	Current Change[d] picoamps	Current Change/ Baseline Noise[e]
5	26.1	.0077	3400	26.0	32000
11	248	.0667	3700	248	110000
21	852	.224	3800	838	260000
33	1700	.368	4600	1700	680000

a   Current at the end of the 200 ppb exposure.

b   Determined from 15 data points over 15 minutes near the end of the 3.75 hour exposure.

c   (Response current)/(response noise), columns 2 and 3, this Table.

d   Response current (this Table) minus baseline current (Table 3, column 2).

e   (Response current change this Table, column 5)/(baseline noise, Table 3, column 3).

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Table 6. Projected Response and Noise Levels at 1 ppb Hydrazine

LB Layers	Current Change[a] picoamps	Total Current[b] picoamps	Total Current/ Baseline Noise[c]	Current Change/ Baseline Noise[d]
5	.130	.219	270	160
11	1.24	1.90	810	530
21	4.19	7.75	2400	1300
33	8.48	14.2	5700	3400

a   (Current change for 200 ppb hydrazine, Table 4, column 5)/200.

b   Current change plus baseline current (Table 3, column 2).

c   (Total current, this Table)/(baseline noise, Table 3, column 3).

d   (Current change, this Table)/baseline noise, Table 3, column 3).

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ratios increase with the number of LB layers, primarily because the baseline currents increase while noise levels are less dependent on the number of layers.

The slopes of the regression lines give a measure of the sensor drift, and are reported as picoamps drift per hour. The values for the 11, 21, and 33 LB layer sensors represent approximately 5% of the baseline current. The drift per hour of the 5 LB layer sensor is only .2% of the baseline current.

To project hydrazine sensitivity down to 1 ppb, the data for the lowest experimental concentration, 200 ppb, were examined. These signal and noise levels are reported in Table 5. By subtracting the baseline currents in Table 4 from the response currents in Table 5, and dividing by the baseline noise in Table 4, one obtains signal to noise ratios of 32000 to 680000 at 200 ppb. The projected current levels at 1 ppb are reported in Table 6. These are calculated simply by dividing the current change due to 200 ppb by 200. The hypothetical signal to noise levels at 1 ppb range from 160 to 3400, and the current levels are well above the drift per hour given in Table 4. Based on this analysis, a new sensor (with baseline characteristics such as those in Table 4) exposed to 1 ppb hydrazine in clean, dry air would give a measurable signal with a large signal to noise.
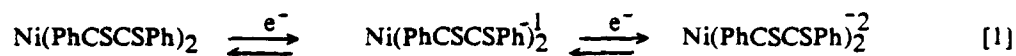
DISCUSSION

The organic semiconductor bis(diethylaminodithiobenzil)nickel, BDN, could be successfully coated onto chemiresistor sensor substrates using the Langmuir-Blodgett technique, provided that the BDN was mixed with stearyl alcohol. The small area per molecule determined from the force-area curves demonstrates that these are not classical films, one molecule thick; the dithiolene molecules must be aggregated. Nevertheless, the LB method has the advantage of providing electrically continuous films with facile control over the amount of material applied. In addition, these films can be very thin. Sensors with as few as five LB layers were fully functional.

The structure of these mixed films has not been investigated. However, they can be compared with mixed LB films containing tetrakis(cumylphenoxy)phthalocyanine (PCCP) and stearyl alcohol (SA). Transmission electron microscope pictures of PCCP:SA 1:1 films have revealed disk-shaped aggregates of PCCP 50-500 nanometers in diameter and approximately 5 nanometers thick, dispersed in stearyl alcohol (32). It is probable that the dithiolene containing films also consist of small crystallites of the dithiolene dispersed in a stearyl alcohol matrix.

The number of LB layers influences several characteristics of the sensors. Fewer layers on the sensor affords slightly faster response times and significantly better recovery. Greater numbers of LB layers give higher baseline conductivities. Baseline noise is least for the 5 LB layer sensor, but shows no trend from 11 to 33 layers. Signal to noise ratios for the baselines and for responses projected at 1 ppb are greatest for the greatest number of layers. Note, however, that as the number of layers is increased, the additional layers are added farther from the sensor electrodes, provide less improvement in baseline conductivity, and degrade response and recovery times. The optimum number of layers will depend on the requirements of the particular application.

Dithiolene-coated sensors gave large responses to hydrazine levels as low as 200 ppb, and sensitivity to ppt levels can be projected. Significantly, the responses to much higher concentrations of ammonia and water were much lower. These results are very promising for the use of the sensors in alarm devices for hydrazine leaks. They are less promising for use in real time monitors for quantifying hydrazine levels because of slow recovery times. The TLV (Threshold Limit Value) for hydrazine is 100 ppb (0.13 mg/m^3), as set by the American Conference on Governmental Industrial Hygienist (ACGIH) (33). NIOSH has recommended a lower value of 30 ppb (34).

The chemical interaction of hydrazine with these sensors must involve reduction of the dithiolene complex. These compounds can be reduced by one or two electrons, electrochemically, or with various chemical reagents.

$$\text{Ni(PhCSCSPh)}_2 \underset{}{\overset{e^-}{\rightleftarrows}} \quad \text{Ni(PhCSCSPh)}_2^{-1} \underset{}{\overset{e^-}{\rightleftarrows}} \quad \text{Ni(PhCSCSPh)}_2^{-2} \qquad [1]$$

The half-wave potentials in DMSO for the first and second reductions are +0.224 V(SCE) and -0.74 V(SCE) respectively (19). The mono-anion can be obtained from the neutral complex using mild reagents such as iodide ion, aliphatic amines, p-phenylenediamine, R_4NOH, or metals such as mercury, copper, aluminum, magnesium, or zinc (19). The dianion can be produced by using sodium amalgam (19) or hydrazine (11). The reaction with hydrazine is given in equation [2].

$$\text{Ni(PhCSCSPh)}_2 \overset{N_2H_4}{\longrightarrow} \quad (N_2H_5{}^+)_2\text{Ni(PhCSCSPh)}_2{}^{2-}(N_2H_4)_2 \qquad [2]$$

A similar reaction has been reported for bis(dimethylaminodithiobenzil)nickel (35). The dianion prepared using sodium amalgam is rapidly oxidized in the solid or in solution to the mono-anion (19). The hydrazinium salt is also reported to be air sensitive, but less so than other salts (11).

Accordingly, exposure of these chemiresistor sensors to hydrazine in air must result in reduction of the BDN to at least the monoanion, and probably to the dianion. Reduction to the dianion by hydrazine, and oxidation by air will be competing processes resulting in some steady state level of reduction. In these processes, the BDN could be regarded as a catalyst for hydrazine oxidation. In clean air after hydrazine exposure, the film will be oxidized to the mono-anion and/or the neutral complex. Trace contaminants in ambient air such as ozone or NO_2 could hasten oxidation to the neutral complex. The fact that these sensors eventually return to the conductivity levels seen prior to hydrazine exposures suggests that they may be oxidized back to the neutral complex.

The increases in conductivity observed on exposure to hydrazine are consistent with the reduction mechanism discussed above. Dithiolenes are n-type semiconductors (13), and in this model, reduction will increase the number of charge carriers. Subsequent

aerial oxidation reduces the charge carriers and conductivity drops. By contrast, phthalocyanines are p-type semiconductors (36). *Sensors using this material increase in conductivity in the presence of oxidizing gases such as* NO_2 *(1,3,5) and decrease in conductivity in the presence of hydrazine (37).*

The response curve of the dithiolene-coated sensors involved a very rapid initial response followed by a slower approach to a steady-state equilibrium response. Chemically, the two different reduced states possible could contribute to the behavior observed. Physically, it is possible that rapid reaction occurs with BDN molecules on the surfaces of crystallites, followed by slower reaction with molecules in the interior as the crystallite structure is disrupted. In the second exposure in Figure 8, the rapid rise in current to the final level obtained slowly in the first exposure is suggestive of such a physical change. The interaction of hydrazine with the film is likely to be complicated, and changes in conductivity may involve both chemical changes in the film material and physical changes in the film structure. DC conductivity in microcrystalline materials is sometimes interpreted in terms of limiting transport of electrons across grain boundaries. In the discussion above, interaction of hydrazine with crystallite surfaces in the LB film could alter electron transport across crystallite boundaries.

Finally, it should be noted that nickel dithiolenes are stable materials. They are extremely photochemically stable and can be used as Q switches in neodymium lasers (20). Thermal stability is indicated by the high 292°C decomposition temperature reported for bis(dithiobenzil)nickel (10) and the report that bis(dimethylaminodithiobenzil)nickel can be vacuum sublimed (38). BDN-coated chemiresistor sensors in our lab have been stored for two and one-half years after fabrication and they behave exactly as expected when exposed to ppb levels of hydrazine.

ACKNOWLEDGEMENT

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